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**Workshop on Nuclear Techniques for Environmental Trace
Element Information Relative to Energy Production and
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Florida State University, Tallahassee. Dept. of Physics

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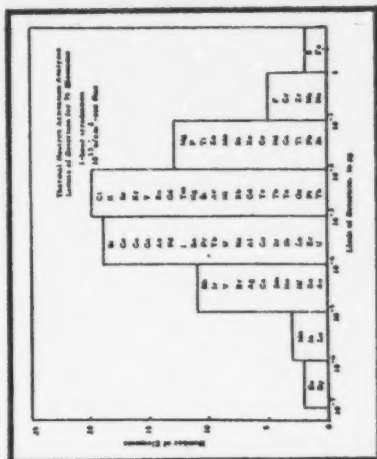
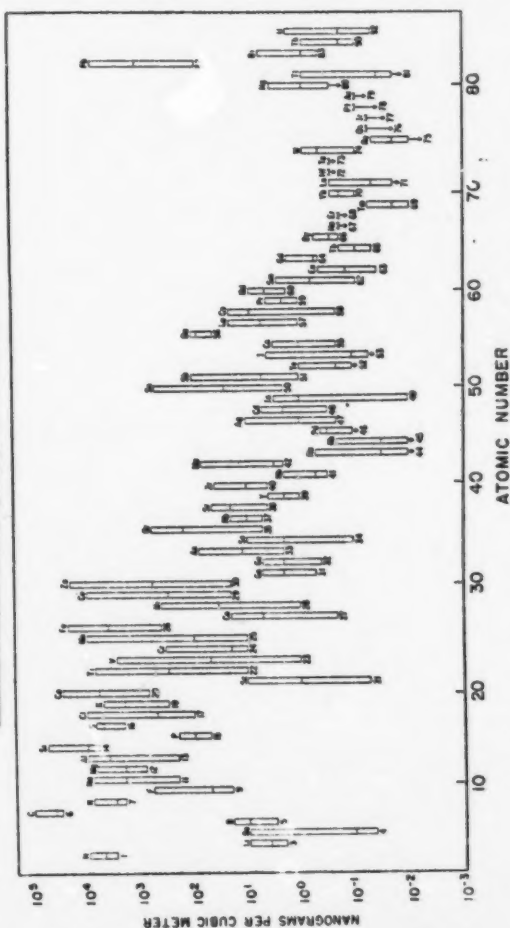
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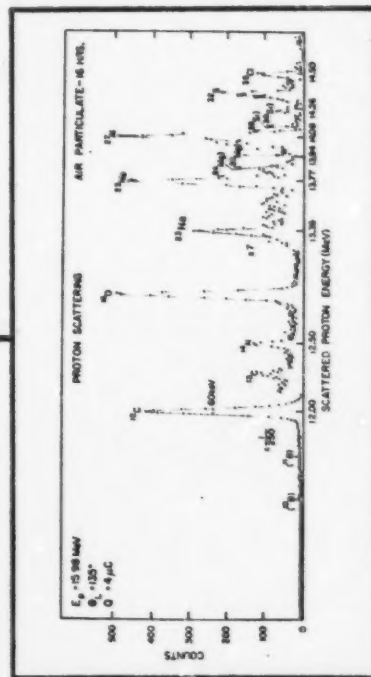
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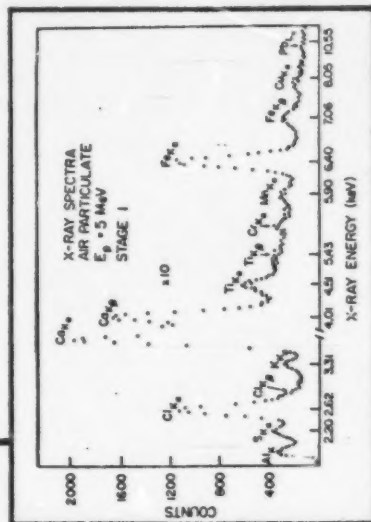
AGROSOB TRACE ELEMENT RANGES AND TYPICAL VALUES



NAA



P-Scattering



X-Ray

(C-CI)

(Al-Pb)

PREFACE

A considerable amount of the motivation for convening this Workshop stems from the recent rapid progress in the sensitive measurement of the elemental content of air particulate matter by automated, broad range, nuclear techniques. As symbolized in the frontispiece, the aerosol is being studied by the multielement techniques of neutron activation analysis, x-ray emission spectroscopy and charged particle scattering analysis. With the combination of these three techniques measurements may be made on all of the elements; however, limits of detection, interferences, etc. limit the actual number observed in any given sample.

While the aerosol problem has received much attention, many other applications for these techniques exist in diverse areas such as analyses of samples of water, biological matter, geological specimens, etc. In addition to the multielement techniques, particular nuclear reactions are being employed for quantitative determination of specific elements or isotopes.

The Workshop was convened for the purpose of discussing these nuclear techniques and their relevance with respect to the problems associated with the production and use of energy and to assess promising avenues of research in this area. The committee wishes to thank the participants for their contributions to both the program and the Workshop report.

Steering Committee:

Tallahassee, Florida
August, 1974

J. William Nelson, Chairman
John W. Winchester
Roland Akselsson

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Part I. Summary of the Workshop

A. Viewpoint of the Workshop

Some 40 scientist with a commitment to environmental trace elements research gathered for three days to discuss the present capabilities and future directions of this research. The group generally had the viewpoint that recent refinements in nuclear techniques for trace elements measurement now make possible new advances in the investigation of the flow of material through the environment and of the impact of trace elements on the biosphere and man. Within the group there was strong representation of nuclear physicists and chemists working actively with x-ray emission techniques for trace element analysis, there was additional representation of nuclear chemists with extensive experience in the application of neutron activation analysis to environmental pollution research, and there were participants concerned directly with national pollution control policy, regional metropolitan energy use planning, and large scale impact of electric power generation on the environment.

The group was firmly of the belief that environmental contamination by trace elements from coal mining, coal and oil combustion, shale oil extraction, and energy intensive industry poses major constraints on our future energy options because of environmental trace element standards. The group clearly saw that nuclear techniques of trace element analysis have already led to major accomplishments in the understanding of the sources and transport of aerosol particles in the atmosphere from natural and pollution origins. The group could foresee equally important future accomplishments in the understanding of the cycling of trace elements throughout the whole environment and their pathways to man. Whereas the group tended to attach great significance to the measurement of the chemical elements, because of the high precision of the measurements currently possible and their value in tracing material flow through the environment, there was realization that an assessment of biochemical impact of trace element pollution on man must include consideration of chemical forms of the elements in the environment. By judicious choice of species specific chemical separation techniques, combined with sensitive nuclear analytical techniques, the careful investigation of this important area was viewed as feasible and one of high priority in the environmental trace elements field.

The liberation into air, water, and soils by energy-production enterprises of trace amounts of radioactive elements may have in some circumstances a degree of importance at least equivalent to that associated with the release of stable elements. This is most certainly a nuclear problem, including nuclear analytical techniques, and its omission from this Workshop reflects the specialities of the participants rather than the significance of the problem

B. Problems Addressed by the Workshop

1. The flow of materials through the environment. The fluxes of energy and matter through the ecosystem are key objects of inquiry among environmental scientists. Because of this, a significance was seen in precise and sensitive trace element measurements as a means to trace the movement of these components from source points through air, water, or the biosphere to their destinations. In a simple sense, clusters of elements in precisely determined proportions may be identified during their transport and followed as to route and rate. Flux information from these substances may lead to projections to other substances more difficult to measure directly. Thus, material balances and flows of trace elements can be of fundamental importance in developing models which describe the pathways of any chemical substances through the environment. However, in order to be useful for this purpose, trace element data must be of high precision and accuracy and often of great sensitivity. Approximate information about the occurrences of trace elements in various parts of the environment may not be very useful in modeling material fluxes. In stressing the accuracy and reliability of trace element measurements by nuclear techniques, the fundamental objective of tracing the flow of matter through natural media was held in mind by many Workshop participants, and in a number of scientific instances nuclear techniques were considered to be the most promising ones to employ in research having this objective.

2. Perturbations by energy-intensive activities. Human industrial activity, whether it be mining the earth for fuels and minerals, liberating heat and ash into the atmosphere during combustion, or manufacturing and degrading the artifacts of technology, may accelerate the flow of matter as well as of energy through the environment. In some reservoirs, such as the atmosphere, bodies of water, or the tissues of organisms, steady state concentrations of certain substances will become elevated if the flow rates in rise faster than the flow rates out. If the health of man or the ecosystem depends on the regulation of these concentrations below certain limits, it is important that we learn to predict with reliability whether new energy-intensive activities may upset natural processes of regulation. Thus, research on the fluxes of trace substances in the environment has an importance much greater than merely assessing their toxic effects. Instead, a full understanding of some trace element flows may provide the basis for forecasting those of other substances. And we may use present anthropogenic perturbations to predict those of the future.

During the post-war nuclear weapons testing years radioactive contamination of the atmosphere and oceans was used to develop models for circulation and exchange which could describe the behavior of many more substances than fission products. Now, with the ability to measure trace elements in environmental samples with great precision and accuracy using nuclear techniques, we can make use of present inputs of industrial dust to the

atmosphere or waste discharges to fresh water and the oceans so as to define pathways of these materials and others with similar environmental properties from their source points to their destinations. If we should discover environmental holdup areas, where concentrations in the steady state should rise greatly above natural levels, we would be guided to examine these further for other biologically important substances which may be dispersed to the environment through human activity. The importance of trace element research using nuclear techniques of analysis, then, lies in our taking advantage of present releases of material during energy production or consumption and the capability for very high quality measurements of the elements as they occur in the environment to define pathways of general ecological importance. Nuclear methods have already been found to be the methods of choice when investigating the elemental composition of pollution and natural aerosols, and indications were also given at the Workshop that nuclear methods may be the methods of choice in similar studies of water and biological material.

3. Trace element impacts on man and the biosphere. Toxicity levels for humans, as well as plant and animal life, of several elements and their compounds have not been established with satisfactory certainty, and there should probably be an early effort in ordering many elements in terms of the importance of need for improved analytical methods and in terms of their probable biological toxicity. Hopefully, standards for drinking water, irrigation water, atmospheric releases, etc., could ultimately be achieved.

A number of trace elements which can be measured accurately by nuclear techniques are of immediate public health interest, and several additional elements potentially also have this interest. Up to the present time, however, biochemical research has been directed more to understanding the relationships and transformations of organic compounds in human physiology than to determining the occurrences of trace elements in tissue, except for certain elements where a significant biochemical role has been established. Also, up to the present time trace element measurements in biological material have been difficult because of the very low concentrations often encountered in vivo and the importance of measurements in samples as small as single cells rather than in larger composites of many tissue types. Consequently, now that we may be on the threshold of greatly increasing the environmental concentrations of some trace elements by increasing our energy intensive activities, we are poorly equipped to predict the consequences for human health and even more poorly equipped to predict the effect on general ecological balance, especially where synergistic effects of several contaminants may be involved.

In comparison with applications to the study of inorganic environmental materials, the use of nuclear techniques in biological or medical research is preliminary. However, exploratory results presented at the Workshop indicated that diseased and healthy human tissues can differ significantly in several elemental concentrations and that environmental exposure to pollution can be

seen by elemental analysis to result in greater body burdens. It appears that several nuclear methods have the sensitivity and contamination control requirements needed to establish these relationships more clearly, and some of them also have the capability for focussing on tissue samples of dimensions as small as a few microns for determinations of elemental constituents at low concentrations in these samples. It is a general consensus of the Workshop participants that refinement of these nuclear techniques and tests of their application to biomedical trace element research should be greatly accelerated. The results may, more directly than in many other approaches, lead to our setting rational constraints on environmental contamination by trace elements.

It is generally realized that biological effects are not caused by elements per se but rather by their chemical compounds, and from an elemental analysis alone it is not always possible to predict the active chemical species. Therefore, many environmental scientists have urged the development of techniques for determining chemical form as well as elemental concentration. With some notable exceptions, nuclear techniques do not give this information directly since the atomic or nuclear radiations detected are not sensitive to the form of chemical bonding. However, chemical species information may be given by a combination of techniques, such as by combining ion etching and ESCA or by chemical treatment of the samples, e.g., by microanalytical separations of different chemical forms, followed by elemental determination in separate fractions by nuclear methods. In radiochemistry the identification of the actinide elements has been achieved by ion exchange separations of ions in aqueous solution and quantitative analysis for the elements by detection of nuclear radiations. A similar marriage of methodology is feasible for many types of environmental samples and is highly recommended by the Workshop. It is essential, if we are to understand the geochemical cycles of trace elements and the extent to which man may be altering those cycles, that we know the chemical speciation of those elements. Further, some effort must be made to understand the rates and mechanisms of inter-conversion of the various chemical species, even if only empirically.

4. The place of trace elements in immediate national environmental missions. Current air quality control needs were presented at the Workshop by representatives of the U.S. Environmental Protection Agency and the Tennessee Valley Authority, and other scientists presented their outlooks for air quality problems resulting from Northeastern expansion of energy consumption and from Western expansion of coal and oil shale production. These are real needs and problems related to the expansion of energy consumption and involve a requirement of trace element monitoring and research leading to predictive models. Nuclear techniques based on x-ray or on neutron-induced radioactivity detection appear at present to be the most successful in providing the quality and quantity of data needed for determining the elemental composition of aerosol particles, especially as a function of particle size. Some saw that this need, great though it is, may be met soon by a reasonably small number of laboratories, thus indicating the

practicality of nuclear applications to this problem area. On the other hand, as our understanding deepens concerning the exact relationships between air quality and public health, the needs for high quality elemental analysis may expand above that currently envisaged. For example, if air quality criteria for particulate matter are set as a function of particle size, composition, and chemical reactivity, the complexity of carrying out monitoring operations could be much greater than at present. In addition, if air quality criteria are set for interior work environments as well as for ambient air, monitoring may become considerably more extensive. Some results presented at the Workshop indicated that the particle size distribution of elemental composition of aerosols in certain operations such as welding may be greatly different from that usually encountered in ambient air, and unusually severe health effects may be caused by elements if they occur on smaller particles than on larger. Documentation of this kind for the many conditions under which people live and work can be a large task, and the facilities and manpower requirements for this should not be underestimated.

Water quality control needs and the needs of ecological quality control involving trace element measurements were presented in much more general terms but appear to be no less real. The Environmental Protection Agency already is seeking for laboratories to provide water analysis service for trace elements, and marine pollution monitoring programs now being developed in several federal agencies will require extensive trace element analysis capability for water, fish, and other materials. Perhaps the greatest need now within the nuclear analysis laboratories is for the development of good techniques for chemically handling, concentrating, and separating trace element components of the samples before their assay by nuclear methods without contamination or loss. This need, however, is considered to be one which will be readily met by teams of analytical chemists and nuclear scientists working together on the problem.

5. Potential for nuclear techniques to meet environmental research and monitoring needs. The most well developed and accepted technique discussed at the Workshop was neutron activation analysis (NAA). Somewhat less accepted, but well along the development road is elemental analysis by x-ray fluorescence. While this technique has been in use for many decades, new life has come into it in recent years due to its simultaneous multi-element analysis capability through use of energy dispersive [Si(Li) detector] or multi-crystal wavelength dispersive methods or a combination of these two techniques. The Workshop participants generally recognized the strongest points of this method as the simultaneous multi-element analysis (with the attendant speed of sample throughput) and the property of being non-destructive of the prepared sample.

Differences in x-ray fluorescence methods do exist but were not a major focus of the Workshop. Excitation of x-rays in a sample may be accomplished by bombardment by x-rays, gamma rays or positive ions. Detection of x-rays may be accomplished with either energy or wavelength dispersive detectors. Various combinations of

these excitation and detection methods may be employed to advantage depending upon the characteristics of particular samples. On the other hand, they all suffer similar self-absorption corrections for thick types of samples. Positive ion beam excitation may be desired to excite a tiny sample, while x-ray or gamma-ray excitation might be preferred for averaging over a sample of larger area. It would be premature at this point in time (and perhaps at any time) to single out any one method or combination as being the best for all applications. It was the general consensus that future developments would define the best methods for different applications but that all represent valid and promising approaches which need help in becoming accepted as general analytical technique

Support in the area of standards is currently needed. Informal, unsupported production of standard samples is presently being carried out. Financial support of efforts in this direction would accelerate the acceptance of this method by scientists who are accustomed to more conventional methods.

Many methods newer than either NAA or x-ray fluorescence were discussed. Charged particle scattering is being used at several laboratories as a broad range technique for the light elements. Used in this way, the scattering represents a complement to x-ray analyses since x-ray analysis is difficult for the light elements. Charged particle inelastic scattering and charged particle nuclear reactions show considerable promise for the detection of specific elements or isotopes in both thin and thick samples.

It was regarded as an important feature that all of these methods may be used in stable element tracer experiments. Furthermore, all of these methods are readily adaptable to automation.

Rapid data acquisition and processing are necessary for nuclear methods to reach their full potential. Standardization of computer methods would be an aid in sharing developments between laboratories. This is already available in software in that FORTRAN is so widely used. In the case of hardware, it was suggested that use of CAMAC interfacing is a method which could meet the need.

Though these many nuclear techniques are in various stages of development, participants presented results showing great potential for further development to produce results beneficial for environmental studies.

6. Evaluation of nuclear techniques for environmental trace element research by examples of aerosol studies. In the Workshop some attention was given to studying the results of certain aerosol research investigations for the information they yielded about the sources and transport of trace elements through the atmosphere. This research serves to indicate the value of nuclear techniques in investigating environmental pathways of

trace elements and to delineate problems in experimental design in studies involving environmental sampling and analysis. Most workers have stressed particulate matter more than the vapor or "molecular" phase, but recent evidence for Pb suggests that the vapor phase may be more important than the particulate in terms of total loading. New techniques of sampling for vapors may be emphasized in future atmospheric trace element research.

An intensive study of particle composition at various points within a coal-fired power plant gave quantitative information about the volatility characteristics and aerosol enrichments of certain trace elements which have previously been found at unaccountably high concentrations in the atmosphere and have been suspected of being of pollution origin. Such a source emissions study is crucial in interpreting ambient air composition measurements and in this case effectively served to direct attention to other sources for explaining many of the previous findings.

The two related studies of ambient aerosol composition in relation to meteorological variables, one in an urban setting and one under unpolluted maritime conditions, indicated the possibility of distinguishing quantitatively between pollution and natural concentration levels of trace elements in aerosols as a function of particle size. Only under certain conditions and for certain elements did the urban area show levels greater than could be accounted for by natural source processes. Thus it is feasible to establish criteria for deciding when a pollutant causes a significant increase in concentration above natural levels in an urban area. Moreover, both studies indicated that vertical transport processes, rather than horizontal transport, may account for a large part of the time variations in concentration seen diurnally or over the course of several days.

In two studies of remote continental western U.S.A. areas, attention was drawn to the potential impact on atmospheric composition by mining and combustion of coal and oil shale. A ranking of importance of trace elements based on potential pollution source strengths and natural atmospheric composition can lead to setting priorities of elements for monitoring possible pollution buildup in the atmosphere. Nuclear techniques were found to be preferred for many of these elements.

In a study of automotive emissions and their dispersion in the urban atmosphere it was found that chronic human exposure in residential areas depended on proximity to freeways, elevation of the freeways relative to ground level, and air circulation patterns. By nuclear analysis methods enough data of sufficient precision could be acquired in a program of reasonable scope and cost to permit urban design and air quality control decisions to be made with much greater understanding than had been previously possible. In this and the other aerosol research experience reported at the Workshop the evidence supported the view that

nuclear techniques are capable of providing the high quality trace element measurements needed for inferring environmental processes.

C. Some Objectives of Federal Funding of Environmental Trace Elements Research

In a time when "relevance" or "significance" of research to national needs is given unprecedented attention by the public and their representatives in government, the objectives of the National Science Foundation and other federal agencies in giving financial support for research should be kept consciously in view. The Workshop considered both short-term missions "relevant" to immediate national needs, such as helping to enforce air quality standards, and longer term missions, such as carrying out "significant" research so that we understand better the environment in which we live. Most Workshop participants perceived the NSF to be the agency most capable to undertake the latter type of mission.

In support of longer term research significant to national needs, two interrelated goals should be kept in view. The first of these is to develop the capability for continuing research in important areas, a goal which is in contrast with the short term goal of some other federal agencies in buying certain specific research results. The second is to encourage the generation of manpower for continuing research progress, such as by training students, facilitating cross-over into environmental science of scientists from neighboring disciplines, and stimulating the collaboration of scientists from different disciplines if this is needed for effective interdisciplinary research. The Workshop participants urge the NSF to give careful consideration to these goals when making its decisions regarding funding of environmentally significant research.

D. The Special Role of Nuclear Scientists in Environmental Trace Elements Research

Results presented at the Workshop indicated that a highly refined capability already exists for carrying out elemental analyses of environmental samples using nuclear techniques with superior sensitivity, precision, accuracy, and general reliability when compared with other analytical methods applied to similar samples. The actual costs of analysis in comparison with some other techniques, especially when measured in terms of environmental information obtained and speed and reliability of analysis, may be less, and any cost comparison should be made only after careful consideration of the objectives of the analytical program.

The present availability of nuclear techniques is, of course, the result of over 30 years of national investment in basic nuclear science research and substantial investment by other countries as well. The possibility of making use of these techniques to study the flows of trace elements through the environment and their impact on man and the biosphere should be perceived as a highly favorable opportunity to derive a substantial benefit from the investment which may not have been foreseen in previous years.

In addition to the direct value of analyses performed by present nuclear methods we may also expect continued advances in nuclear analytical methodology which may open up new horizons in environmental research, providing that the necessary funding is allocated both in applications oriented fundamental research and in the development effort required to go from a benchtop, laboratory method to a reliable technique accessible to people outside the nuclear area.

It is noteworthy that the nuclear scientists now engaged in environmental trace elements research have a personal commitment to obtaining the highest quality analytical data. An effective interlaboratory comparison of several related nuclear techniques of elemental analysis was reported in August 1973 and a second is scheduled for reporting in August 1974, with a preliminary report given at the Workshop. Not only did the results of these comparisons show a much greater degree of agreement among investigators and with true values than is customary in similar intercomparisons of environmental chemical analysis techniques using non-nuclear methods, but the fact of conducting such intercomparisons at all, without the explicit encouragement or support of a federal granting agency, shows an unusual awareness of the importance of such an exercise in assuring high quality analytical data. In both respects, then, the successful interlaboratory comparison studies can be considered a major achievement.

Through the effective cooperation in the intercomparison exercises and in the general degree of interlaboratory communication which already exists in the nuclear science group represented at the Workshop, the group appears to have a good level of critical mass interaction among its members which may lead to rapid development of scientific research on environmental trace element pathways and effects. Mutual interest among the investigators has already moved beyond the analytical techniques employed and into the environmental research area. Such interaction should be encouraged for this is the means for developing the capability for continuing research beyond any short term goals of the present.

Scientists with experience in interdisciplinary environmental research generally agree that they must each one make a total commitment to the environmental research objective to which they are applying their special skills or techniques. Within any team of investigators, where there may be specialists in each of the pertinent disciplines, there develops an interdependence so that each member may rely on the other for this expertise. Nevertheless, each member views himself as committed to achieving the environmental research goal of the team, not merely carrying out his specialized function for the team. For the nuclear science group gathered in the Workshop there were

many indications that the investigators have made the transfer of identification from their original specialty of physics, chemistry, or other basic field to the environmental field, e.g., air quality, biomedical, or water research. The ability of members of this group to make this transfer of personal identification may be the single most favorable indication of a long term commitment to succeed in environmental trace elements research. Therefore, we may expect that they will bring far greater resources to bear on the research than the analytical skills of their nuclear methods, for they will apply the whole range of intellectual discipline of their basic scientific training to the central environmental problem. This is a matter of the utmost importance to a federal agency concerned with guiding future scientific work into new avenues of national significance.

Part II. Technical Summaries of Workshop Discussions

Air Pollution Research Objectives Using Neutron Activation Analysis

Vincent P. Guinn, Department of Chemistry, University of Calif., Irvine

It is well known that study of environmental trace elements in samples of air particulates* (and of waters and biological materials) requires analytical methods of high sensitivity, since the element concentrations of interest are either quite low--in many cases being in the range of ppb to ppm in the samples to be analyzed, or the samples are very small. In environmental studies, the analytical method characteristics of precision, accuracy, multi-element capability, speed, and low cost are also of importance. Experience of the author, and of many others, shows that reactor-flux thermal-neutron activation analysis (NAA) is an outstanding method of trace-element analysis in all these respects (although of course, it is not the method of choice for every kind of sample or study--just as no other single analytical method is either).

The method of NAA typically involves the exposure of from one to many samples and standards to a thermal-neutron flux of the order of 10^{13} n/cm²-sec for one or more selected periods of time, with subsequent counting of the activated specimens, at one or more selected decay times--usually with a Ge(Li) multichannel gamma-ray spectrometer (for certain elements in some matrices, post-irradiation radiochemical separations with carriers are necessary before counting, but many environmental studies only require the purely instrumental, nondestructive, form of the method). Under typical conditions, the NAA method provides outstanding sensitivities of detection for the majority of the elements of the periodic system. In the absence of interferences, these lower limits of detection range from as low as 10^{-7} μ g (for few ultra-sensitive elements) to a median of 0.001 μ g, to as high as 10 μ g (for a few rather insensitive elements). Sample sizes can typically range from micrograms up to as much as a gram (for a 1-gram sample, the μ g limits are then numerically the same as the ppm limits). In complex matrices, many elements present in the sample become significantly radioactive, as the result of neutron capture, and the actual lower limit of instrumental NAA detection may be thus raised, in some cases, to levels 10 to 100 times their interference-free limits, whereas others are affected very little. At levels appreciably above the limits of detection, precisions and accuracies approach $\pm 1\%$ of the value.

In instrumental studies of such environmental sample materials as air particulates, coal, petroleum, ocean sediments, and biological materials (e.g., fish, hair, plants, etc.), various workers, including the author, have shown that anywhere from 15 to 35 trace elements can be detected, firmly identified, and quantitatively measured in each sample.

*In this summary, the term "air particulants" is used in the broadest sense, i.e., to include all suspended solid particles--from the smallest filterable aerosol particles on up to very large particles that readily settle out even without filtering.

Analysis time can range all the way from seconds per sample, if only very short-lived induced activities are measured (e.g., 0.80-second ^{207}Pb , 11.56-second ^{20}F); to a minute or two per sample, if slightly longer-lived species are measured (e.g., 24.4-second ^{110}Ag , 2.31-minute ^{28}Al , 3.75-minute ^{52}V); on up to many minutes or a few hours per sample, if long-lived activities are measured (e.g., 12.80-hour ^{64}Cu , 13.8-hour $^{69\text{m}}\text{Zn}$, 26.4 hour ^{76}As). However, especially in the latter case, a large number of samples can be activated simultaneously, and many elements detected and measured in a single counting period--so the time per element is still small.

NAA has already made many important contributions to our knowledge of air and water pollution problems, but it has far greater potential than has yet been tapped. It complements such other methods as x-ray fluorescence/emission and atomic absorption. It can aid greatly in investigations of elemental baseline levels, sources of elemental pollutants, and the pathways in the environment of various elemental pollutants.

Summary on Air Pollution Research at TVA

Chao-Ming Huang, Tennessee Valley Authority, Muscle Shoals, Ala.

TVA has been engaged in air quality research and control for more than twenty years. Much of the findings and techniques developed by TVA for field research, air quality monitoring, and air pollution control have found wide use throughout the country. This presentation will be concerned only with four categories of TVA's research activities. (1) Research on the effects of SO_x , including examining the effects of exposing vegetation to SO_2 and stack gases and to filtered and unfiltered air; conducting field surveys to determine the effects of power plant operation on growth and timber yield of forests and of leaf injury on yields of soybean plants; conducting atmospheric chemistry studies to ascertain the interactions and fate of various constituents of power plant emissions. (2) Research on particulates, including participation in a study conducted at TVA's Allen Steam Plant by the Oak Ridge National Laboratory in an effort to obtain a mass balance of trace elements, particle size distribution of fly ash, correlation between trace element content with particle size of fly ash, and to ascertain the fate of discharges of these elements and the effects of particulate fallout on the environment; analysis of sulfate content of suspended particulates collected in the vicinity of TVA power plants. (3) Research on NO_x emissions, including participation in the Esso/EPA studies to investigate methods for controlling NO_x emissions from utility boilers; measurement of NO_x emissions from different types of TVA fossil-fuel-fired boilers and combustion turbines; evaluation of NO_x production due to arcing of electrostatic precipitators; studies

of effects of burning low sulfur coal in NO_x emissions; studies to determine the applicability of specific combustion modification techniques and their effects on NO_x and other pollutant emissions and on the operation and performance of utility boilers.

(4) Research on control of SO_2 emissions, including field studies to develop dispersion techniques for controlling SO_2 emissions, research with fundamental chemistry and bench-scale processes for removing SO_2 from stack gases; pilot-, prototype-, and full-scale testing of several SO_2 removal technologies; design and construction of a full-scale limestone scrubber at TVA's 550-MW Widows Creek unit 8 boiler; testing with low sulfur coal.

Interlaboratory Comparison of Trace Element Analytical Results*

David C. Camp, Lawrence Livermore Laboratory, Livermore, Calif.

How accurately can x-ray fluorescence (XRF) and other analytical techniques determine trace element concentrations in aerosol particulate samples? To help answer this question, an intercomparison of the analyses of well characterized samples has been carried out. Samples were analyzed by some six different analytical techniques at about twenty laboratories worldwide. Columbia Scientific Industries (CSI) prepared two types of "standard" samples. The Environmental Protection Agency (EPA) obtained real aerosol samples. The objective of the study was an intercomparison of the precision and accuracies resulting from the various analytical techniques used to determine the trace element content. Particular emphasis in this second intercomparison was addressed to spectral interferences, self-absorption, and particle size effects.

Three types of samples were provided. A known volume of a ten-element solution was deposited by a multidrop technique onto 47 mm diameter Millipore cellulose membrane filters and then dried. The elements deposited were Al, S, K, V, Cr, Mn, Fe, Zn, Au, and Cd, and their concentrations varied from 1 to 100 $\mu\text{g}/\text{cm}^2$. The second type of sample was prepared from a standard rock. The rock powder was homogeneously deposited on similar Millipore filters by the puff technique and sealed with a 30 $\mu\text{g}/\text{cm}^2$ layer of paraffin wax to prevent losses of the small particles. About 30% of the particle sizes were in each of the three ranges: 40-20 μm , 20-10 μm , and 10-1 μm . The remainder were less than 1 μm . The most common elements found in the rock samples were Al, Si, K, Ca, Ti, Mn, and Fe. The mass per unit area deposited varied from 200 to 500 $\mu\text{g}/\text{cm}^2$. The third type of sample consisted of aerosol particulates gathered by the EPA. These had loadings of approximately 370 to 510 $\mu\text{g}/\text{cm}^2$. Typical elements reported were Al, Si, Fe, S, K, Ca, Ti, Se, V, Mn, Sr, Br, Ba, As, and Pb. Two samples of each type, where possible, were sent to the participants.

*Supported in part by the auspices of the U.S. Atomic Energy Commission.

The six analytical techniques used were (1) proton and alpha particle XRF, (2) radioactive source, tube-excited, and secondary-excited XRF, (3) wavelength dispersive XRF, (4) neutron activation analysis, (5) atomic absorption spectroscopy, and (6) emission spectrography.

All of the solution rock, and particulate samples were monitored by XRF at CSI before being sent to each investigator. Those returned will be similarly monitored to check for any changes. A quality control set of six filters plus blanks remained at CSI. Preliminary results reported at the Workshop indicate that this intercomparison is more successful than the first. Results will be presented at the Denver X-Ray Conference, August 9, 1974.

Aerosol Composition Studies Using Accelerator Proton Bombardment

The Aerosol Elemental Analysis Group*, Florida State Univ., Tallahassee

The proton beam of a Van de Graaff accelerator serves as an intense excitation source for elemental analysis of small thin samples $\leq 5 \text{ mg/cm}^2$ contained within the few mm^2 dimensions of the beam. In proton induced x-ray emission (PIXE) the characteristic K x-rays of the elements from S to Br and heavier and the L x-rays of the heaviest elements up to Pb and beyond are generated using 4 MeV protons and are detected by a Si(Li) detector, and the spectrum of a few minutes bombardment is recorded on magnetic tape for computer data processing. The procedure is now routine, and 100 or more samples can be analyzed in 24 hours of accelerator time. By a separate bombardment using 16 MeV protons the elastically scattered proton spectrum, detected by a Si detector, permits resolution of light elements, including Li and C, up to S and beyond. The procedure (PESA) is under development but shows promise for a complete analysis of the same sample for the lightest elements to the heaviest by combining the two techniques.

Application to the study of the elemental composition of aerosol particles is straightforward and permits determinations both of the variation of composition with particle size, by sampling with cascade impactors, and of time variation of composition using a time sequence filter sampling device. Studies of ambient air

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in urban and remote areas, atmospheres of indoor work environments, and the uptake of aerosol particles by human subjects during breathing are in progress. Impactors with a single orifice per stage and operating at atmospheric or reduced pressure give size resolution down to 0.25 μm or below and small sample deposits on thin films suitable for proton beam bombardment. A special filter sampler with a moving sucking orifice produces a continuous streak over a 7 day period on a single Nuclepore filter strip permitting rapid and automated sequential analysis with 2-hour sampling time resolution. The same streak can also be analyzed for total mass by beta particle transmission using a C-14 source. By combining these nuclear measurements for aerosols, a determination may be made of all their important elemental constituents.

The techniques are currently being regularly employed in the St. Louis Regional Air Pollution Study of the U.S. Environmental Protection Agency, and the elemental composition of the St. Louis aerosol has been investigated at rooftop sites in south and central locations in the city as part of the August 1973 field season. The aerosol study indicates the following:

1. Particle size distributions of S, Cl, K, Ca, Ti, V, Mn, Fe, Cu, Zn, Br, and Pb can be measured in samples from 0.7 m^3 of air collected over 12-hour intervals at 1 liter/min flow rate, with precision of single analyses generally 10-30% except near the nanogram detection limit.

2. Some elements, e.g. Ca, Fe, Ti, K, show a tendency for highest concentrations in air measured in largest particle size fractions, and the pattern of distribution of concentration with size is relatively invariant. Predominantly dispersion source processes may account for their entry into the atmosphere.

3. Other elements, e.g. S, Pb, Zn, have substantial proportions of their atmospheric concentrations on smallest particles and show greater variability in particle size distribution patterns, suggesting aerosol formation processes of vapor condensation at high or low temperatures.

4. During 16-22 August 1973 an atmospheric change occurred from a period of low speed and mostly southerly air flow, with evident haze and air pollution, to higher speed and westerly shifting to easterly air flow, with improved visibility and air quality. The change was associated with drops in concentrations of Ti, Fe, Ca, K, and S but not Zn or Pb at the south site and Ti but not the other elements at the central site. Transport of air pollution from industrial sources south of the city is indicated.

5. The central site showed diurnal variations during the first period where concentrations of Ti, Fe, Ca, K, and S were higher in samples taken from midnight to noon than those from noon to midnight. Variations were greatest for intermediate sized particles.

Concepts for a Large-Scale Aerosol Particulate
Collection and Analysis System*

J. M. Jaklevic, F. S. Goulding and B. W. Loo, Lawrence Berkeley
Laboratory, Univ. of California, Berkeley

This talk dealt with the design features of a multiple station air particulate sampling network being built at Lawrence Berkeley Laboratory for use in the Environmental Protection Agency St. Louis RAPS study. The objective of the network is to obtain total mass and elemental composition for size segregated aerosol particulates. The sample collection, analysis and subsequent data handling are designed to be fully automatic for use in very large-scale monitoring programs.

Previous work has established the existence of a bimodal particulate size distributions in urban aerosols and has related the individual modes to distinct formation mechanisms. Information obtained for the individual size fractions could then be correlated with the relative contributions of various energy related pollution sources. The goal of the sampling network is to monitor the composition of each fraction independently by depositing the respective size ranges on a membrane type filter. The analytical methods employed in the subsequent analysis are beta-gauging for the total mass and photon-excited energy dispersive x-ray fluorescence analysis for the elemental composition. The x-ray fluorescence method employed has been under continuing development at LBL for the past several years. An automatic XRF system design and constructed under contract with the EPA has been in successful operation at Research Triangle Park, North Carolina over the past 1.5 years.

A unique feature of the automatic air sampler is a virtual impactor which aerodynamically separates the incoming airstream into two fractions each carrying particles either above or below some predetermined cutoff diameter (typically 2 μm). The particulate material from each airstream is then deposited uniformly on a membrane filter for subsequent analysis. Measurements with a prototype device indicates minimal wall loss and particle bounce-off problems. This is in contrast to conventional size separating impactors when the re-entrainment of deposited particles results in considerable uncertainty in the interpretation of size-distribution data.

The completely automatic sampling stations are in the process of construction. The electronic timer and controller for the air samplers are designed to be operated either via a central computer or individually in a fully automatic mode. Considerable

*This work was supported in part by the Environmental Protection Agency under Interagency Agreement with the U.S. Atomic Energy Commission Contract No. EPA-IAG-D4-0377.

attention has been devoted to the reliability and operating conveniences of the monitoring operation and subsequent data handling stages. In view of the large number of samples generated by such a network, a computer oriented data handling system has been devised including computer readable digital identification code for each filter.

The combination of semiconductor detector technology, pulse electronics, and computer systems represent the convergence of a number of technologies which have been developed to a high level of sophistication in the nuclear field and are now being used to advantage on environmental type problems. The successful development of the virtual impactor and associated air sampling hardware illustrates how these technologies can lead into other programs of interest and relevance.

Significance of Remote Marine Aerosol Studies in Energy Impact Assessment

Dennis L. Meinert, Dept. of Oceanography, Florida State Univ., Tallahassee. Present address: Tennessee Valley Authority

On Bermuda from a 50-meter altitude and over the North Atlantic Ocean from shipboard, cascade impactors were used to collect particle size fractions of the natural aerosol. The elemental abundances of 10 elements, S, Cl, K, Ca, Ti, Mn, Fe, Zn, Br and Pb, determined by proton-induced x-ray emission (PIXE) spectroscopy, were studied as a function of particle size.

The absolute concentrations of "chlorine type" elements, i.e. those associated with a marine origin such as large particle S, Cl and Br, in general, varied inversely in relation to the absolute concentrations of "iron type" elements, i.e., those associated with the general tropospheric aerosol and of a terrestrial origin such as Ti, Fe, and Pb. It is well acknowledged that the major source of particulate chlorine in the atmosphere is the process of bubbles bursting at the air-sea interface injecting sea-salt particles into the air to be carried off by the wind. Therefore, aerosols sampled under conditions when the seas are roughest and winds highest will exhibit the greatest concentration of "Cl type" elements. On the other hand, "Fe type" elements are not of a marine origin but are part of the general tropospheric aerosol, containing components of a land origin. A simple model for the aerosol in a marine environment, up to 100 meters, would be one in which the source of "Fe type" elements is from above, the troposphere, and the source of "Cl type" elements is from below, the sea surface. Under rough weather conditions vertical turbulent mixing may increase the thickness of the atmospheric boundary layer over the sea surface resulting in an increased efficiency of washout of tropospheric "Fe type" elements. At the same time the concentration of elements generated at the sea surface is being increased. Under calmer conditions, the downward mixing and

gravitational deposition of "Fe type" elements which are present in the general tropospheric aerosol results in a greater contribution to the sampled aerosol from elements of a tropospheric origin while at the same time input from the sea surface is diminished. Consequently, local meteorological conditions during sample collection greatly influence the relative contributions of sea surface and tropospheric sources to the air at the sampling site.

Assuming that the majority of the chlorine was of a marine origin and the majority of the iron was of a tropospheric and ultimately of a terrestrial origin, the data were grouped into two sets, viz. high Cl/Fe ratios and low Cl/Fe ratios. As a result the high Cl/Fe ratio set generally correlated with windy, rainy weather and was strongly influenced by sources at the sea surface. The low Cl/Fe ratios set correlated with calmer weather conditions as was more influenced by the general tropospheric aerosol.

Fe, Ca, Cl and Br were found mainly on large particles suggesting a mechanical generation process such as soil dispersion or rupturing bubbles at the sea surface. Pb, when present, was found only on smaller particles suggesting a vapor condensation source process. Mn had an intermediate size distribution pattern showing no consistent preference for large or small particles.

Detailed examination of size distribution patterns suggests that large particle K and Ca originate from both a marine and land environment. Evidence is presented which suggests that small particle K has an additional small particle, non-marine source.

Ti which is basically large particle oriented may also have an additional small particle, non-marine source.

The distribution of S was distinctly bimodal. The large particle S is most likely SO_4 of a marine origin while the small particle S could be the result of a secondary conversion process in which H_2S and/or SO_2 gas is oxidized and converted to small particle SO_4 .

Anomalously high concentrations of zinc were recorded. The Zn data suggest that a marine environment may be a source of large particle Zn, perhaps a result of ion fractionation at the air-sea interface. The data also suggest a small particle source of Zn not associated with a marine environment.

Environmental Sampling in a Remote Area*

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The Rocky Mountain area in the states of Wyoming, Utah, Colorado, Arizona and New Mexico is a sparsely populated, arid country of extreme weather conditions but an area of color, changing terrain, and wild beauty. This area is known to contain vast stores of natural resources including 800 billion tons of coal,¹ oil shale bearing 1800 billion barrels of oil,² significant uranium deposits, and conventional gas and oil deposits. These energy related resources are being developed for transport to other parts of the country as well as for conversion to power within the intermountain region.^{1,2} Increasing development of resources will have significant impact on this remote area.

There are two important reasons for extensive environmental studies in remote areas of the Rocky Mountain region (as well as in other remote areas). First, such studies will provide information relative to natural ecosystem patterns in an environment unpolluted by man's activities. Second, such studies are necessary in order to evaluate the impact of energy development.

Reference to the Southwest Energy Study¹ indicates the significant trace element content of coal to be burned in the thermoelectric power plants planned for the Southwest. Trace element studies of air, water, soil, plants, and animals are an important aspect of required environmental studies. Such is particularly needed in the local regions about mining and power plant operations.

The Anderson mini-sampler or personnel monitor has been used as a basis for a remote-area, air-particulate sampling device. The sampling head has four particulate impaction stages followed by a Nuclepore back-up filter. The device has the following characteristics: (1) Self-contained power supply, (2) The capability for two to three weeks continuous operation, (3) Particulate size discrimination for the separation of large and small dust particles allowing a maximum sensitivity for small particle power plant emissions, and (4) Samples are suitable for elemental analysis by proton-induced x-ray fluorescence. This instrument is being used to collect air particulate samples in the region west of Lake Power--a Colorado River lake. The proposed Kaiparowits Power

*This work was supported in part by a grant from the consortium of companies with interest in the Navajo and the proposed Kaiparowits Generating Stations.

¹Southwest Energy Study, An Evaluation of Coal-Fired Electric Power Generation in the Southwest, U.S. Dept. of Interior (Draft) April, 1972.

²Final Environmental Statement for the Prototype Oil Leasing Program, U.S. Dept. of Interior, August 1973.

Station may be located in this region. X-ray fluorescence analysis of the particulates indicate significant enrichment of nickel, zinc, lead, and perhaps arsenic and selenium with respect to average crustal abundances of these elements.³

In addition to air-particulate trace-element analysis, soils, plant material, small animal tissue, and surface water are also being analyzed for trace-element content. These data will be evaluated together with meteorological and biological data collected in the same regions.⁴

A few suggestions for other measurements important in this region and which involve nuclear techniques are the following: Measurement of total radioactivity, including alpha activity, in order to evaluate the importance of radon and uranium emitted in power plant operation. The use of radioactive and of non-radioactive tracers for the evaluation of wind-flow patterns at proposed power plant sites. The use of nuclear methods in the evaluation of archaeological findings and the determination of air-borne fluorine concentration.

Power Plant Impacts on the Urban Aerosol

E. Gladney, Dept. of Chemistry, Univ. of Maryland, College Park

Elemental compositions of the coal, various ash fractions, and suspended particles in the stack of the Chalk Point (coal-fired) power plant in southern Prince George's County, Maryland have been measured by instrumental nuclear activation methods. Similar analyses were performed on ambient particulate samples collected at ground level by a network of stations near the plant and with a mobile sampling vehicle equipped with an SO₂ analyzer and condensation nuclei counter to detect the plume. This particular plant appears to cause less enrichment of moderately volatile elements on suspended particles in the stack (with respect to the input coal) than plants studied by other U.S. groups. The enrichment factors (with respect to the earth's crust) of most elements on the emitted particles are rather similar to values observed for background ambient particles in the area. Thus, emissions from the plant raise the ambient concentrations of most elements on particles rather uniformly without greatly altering the pattern of relative concentrations.

³ K. H. Wedepohl, "Chemical Fractionation in the Sedimentary Environment", Origin and Distribution of the Elements, L. H. Ahrens, ed., (Pergamon Press, London, 1968) pp. 999-1016.

⁴ N. F. Mangelson, G. M. Allison, D. J. Eatough, M. W. Hill, R. M. Izatt, J. J. Christensen, J. R. Murdock, K. K. Nielson, and S. L. Welsh, "Trace Element Analysis for the Environmental Baseline Studies of the Navajo-Kaiparowits Generating Stations", Trace Substances in Environmental Health-VII, Delbert D. Hemphill, ed., (University of Missouri, 1973).

Trace Elements and Energy Resources--Nuclear Methods of Analysis

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Several techniques of nuclear physics commonly available in a nuclear physics laboratory equipped with a variable energy cyclotron have been applied to problems of trace elements associated with energy production. In particular, by the method of observing gamma rays following inelastic proton scattering, we have been able to measure fluorine down to 10 nanogram amounts, and we have measured boron concentrations in solid samples down to 100 ppm by use of the $^{10}\text{B}(p,\alpha)$ reaction. Fission-fragment trace detectors are being employed in an effort to determine the spatial distribution of plutonium in air filter samples with fission being induced by thermal neutrons and by 36-MeV alpha particles. Trace element studies using x-ray fluorescence and radioactive counting techniques are underway for stable and radioactive trace elements in coal from throughout the western United States and in oil shale from the Green River Formation in Colorado.

Contributions of Freeway Traffic to Airborne Particulate Matter*

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Particulate matter was collected in the vicinity of freeway sections in the Los Angeles basin in order to study the nature of traffic-generated particulate matter, to ascertain precise sources, and to examine dispersion patterns as a function of traffic, weather, and roadbed configuration. Four stage Lundgren impactors with afterfilters provided information on particle size while generating samples suited to the ion-excited x-ray emission based elemental analysis system of the University of California, Davis.¹ Over 3,000 samples were collected and analyzed, with the area background subtracted from the freeway source by upwind/downwind sampling arrays.

The traffic generated particulate matter correlated well with automotive and roadbed expendables. Dispersion patterns showed lower values for particulates downwind of depressed freeways than at-grade or, especially, raised freeways. Lead levels greatly exceeded existing state standards if values seen during this study were typical.

These freeway data were then compared with results from the ARB study, Regional Monitoring of Smog Aerosols, also based

*Work supported by the California Air Resources Board (ARB)

¹Built with ARB and NSF/RANN support.

at UCD. If the data for Los Angeles for summer, 1973, is ratioed to lead and compared with the freeway source, the contribution of automotive traffic to local aerosols can be estimated. For elements sodium and heavier, in particles less than 20 μm diameter, the approximate source strengths are:

<u>Sources</u>	<u>Source Strength</u>	<u>Major Elements</u>
Power Plants & Petrochemicals	36%	S, V, Ni
Automotive	28%	Pb, Br, Fe, Si, S, Ca, Cl, Al, Zn, K, Cu
Soil Derived	25%	Si, Fe, Al, Ca, K, Ti, Mn
Sea Salt	7%	Na, Cl, (Mg, S)
Other	5%	K, Zn, (Mg), Ti, Mn, Cu
	<u>100%</u>	

Major "Deficits"

Chlorine	-10%	Elements that appear to have gone into
Bromine	- 2%	the gas phase, based on mass balances.

These elements represent, however, only about 8% of the particulate matter seen at Los Angeles. The major missing factors are elements C, O, N, and H (~80% of the mass), and large soil particles (~12% of the mass).

Elemental Analysis with Nuclear Techniques *

B. L. Cohen, Dept. of Physics, Univ. of Pittsburgh, Pennsylvania

Filter brushings--The basic composition of air particulate has not been studied as a function of time and location due to difficulties in chemical analysis of small samples. A method was developed using prompt gamma rays induced by proton beams on dust brushed from filters. It gives high accuracy (~5%), requires only 200 mg of sample, and determinations for 8 elements (C, N, O, Al, Si, S, K, Ca, Fe) can be done for \$15 per sample in large batches (Analytical Chem. 45, 284 (1973)).

Pb/Fe Ratios in Pittsburgh Air Particulate--Studies of air particulate collected by sucking air at 6 liters/min through nuclepore filters and analysed by PIXE indicate that measurements of this type on the Pb/Fe ratio can be used to determine whether automotive or industrial sources (or both) are responsible for air pollution alerts in Pittsburgh (Env. Sc. and Tech., in print).

*Principal collaborators in this work were G. Wedberg, K. C. Chan, L. Shabason, and J. O. Frohlinger.

Comparison of Rainwater Analyses in Pittsburgh and Rural West Virginia--Rainwater collections from 26 rainfalls in rural W. Va. and 13 rainfalls in Pittsburgh were analyzed by PIXE and compared. Variations in rainwater samples are much wider than in air particulate samples, but it is hoped that comparisons of averages of a large number of samples from different areas are meaningful. Total solids in Pittsburgh rainwater average several times higher, and each element studied was higher except for phosphorus. Heavy metals are relatively more important in Pittsburgh. In both locales Cu was much more prominent than in air particulate (Paper in preparation).

Thick Sample Analysis by PIXE--In attempting to apply PIXE to analysis of coal and ash, difficulties were encountered in preparation of thin samples so a thick sample technique was developed using 0^{16} ion excitation to achieve equivalent thinness from the range of the incident beam. It was shown that the x-ray absorption is the same as if all reactions take place at 21% of the incident ion range, and from this, limiting 0^{16} energies were calculated. Background x-rays from charge build-up on the thick, insulating samples were eliminated by introduction of a hot filament. Resolution is slightly poorer because of complex excitations induced by heavy ions. (Jour. Applied Phys. 44, 4749 (1973).)

Trace Analysis and Depth Profile Studies of Hydrogen--Analysis for hydrogen by coincident detection of the two protons from p-p scattering was developed. Where sample thickness is uniform, measurement of the summed energy of the two protons determines the depth within the sample at which the hydrogen is located (Jour. Applied Physics 43, 19 (1972)). The method has recently been applied to studies of hydrogen in glass (with R. deSalvo, Penn State), aluminum (with H. Leidheiser, Lehigh Univ.), and silicon (K. Mayer, Siemens). Sensitivity has been pushed down to 0.5 ppm atomic, or 20 ppb by weight. (Paper in preparation.)

Water Pollution Research Objectives using X-Ray Methods of Trace Element Analysis

J. R. Rhodes, Columbia Scientific Industries, Austin, Texas

In contrast to air particulates analysis, the use of x-ray emission spectrometry (XRF) for multielement trace analysis of suspended or dissolved solids in water requires significant sample preparation. It is also no more sensitive than other techniques in routine use such as atomic absorption (AA), emission spectrometry (ES) and polarography. An economic case must therefore be made for employing XRF in preference to the other techniques.

The salient features of XRF are: (1) Multielement, qualitative and quantitative (especially the energy dispersive versions); (2) Rapid, easily automated; (3) Suited to thin

specimen analysis (yielding minimal interferences, linear response and optimum sensitivity) which facilitates sample preparation; and (4) Nondestructive to the analyzed specimen.

A cost benefit analysis performed in 1971 indicated that, for routine determination of 15 elements/sample the XRF cost was estimated at approximately \$0.80/element, of which about 50% is for sample preparation (preconcentration and formation of the thin specimen). Comparative costs for AA and ES vary from \$1.27 to \$4.16/element, and even up to \$12.50/element in one case. Also one XRF instrument can easily handle 100 samples/day whereas the rate for routine multielement analysis by the other methods is an order of magnitude lower. However, the XRF analysis cost per sample does not vary much with the number of elements per sample determined, yielding for example a cost per element of \$3.00 for 4 elements/sample. The place for XRF is, therefore, in large multi-sample, multielement analysis programs.

Significant development work is required to optimize preconcentration techniques and match them to the requirements of XRF. Of the main preconcentration techniques, viz., precipitation, co-precipitation, filtration, ion exchange, liquid-liquid extraction, electrochemical, chromatography, evaporation, sublimation, distillation, carbon adsorption, and the use of membranes (e.g., osmosis, dialysis), only ion exchange and precipitation/co-precipitation have been thoroughly investigated and even these have not been completely explored in the context of energy dispersive XRF.

Since the abovementioned economic advantage of XRF depends on the optimization of the preconcentration and sample preparation procedure, this is where the development effort ought to go. We recommend that two to four specific R & D projects, each of about 1 man-year's magnitude, should be funded in this area. The choice of project should be made with reference to pending large water analysis programs at, for example, EPA, USGS, NOAA and OWRR. This work would naturally be followed by intercomparison studies between laboratories and between techniques.

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Energy Related Trace Elements in Biological System

Poen S. Ong, Univ. of Texas System Cancer Center, M. D. Anderson Hospital and Tumor Institute, Houston

The trace metals of interest in biomedical research may be divided into two categories, i.e., the essential and nonessential elements. To the last group belong also the toxic elements, of which several are found in air as industrial pollutants. Toxic metals tend to replace the essential metals belonging to the same group of the periodic table. Since the essential trace metals form the center of enzymatic activity, these activities could therefore be impaired. The study of the biological effect of toxic metals requires the identification of the protein effected, and the evaluation of the degree of substitution and its effects on metabolic and enzymatic activity. There are presently no established methods which permit such a study and the need for the required technology is urgent.

The approach to be followed in the Section of Experimental Pathology at M. D. Anderson Hospital is to separate the protein to its components followed by the trace metal characterization of each fraction. This technique, using column separation and x-ray fluorescence analysis, is being developed in the Laboratory for Bioanalytical Physics.

In addition, since electrophoresis is a well established technique requiring a minimum amount of preparation, the resulting cellulose strips could be analyzed for metal content and allow identification of the effected protein. An instrument using a line focused x-ray monochromator as an excitation source is being built and tested to be used for such a study. This particular research program is supported by a grant from The Robert A. Welch Foundation, No. G-545.

Trace Elements in Human Health

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Our experience (and that of several other laboratories) shows that proton induced x-ray emission spectroscopy is a multi-element technique of trace analysis with uniformly high sensitivity for all elements heavier than sodium. Most samples can be analyzed for quantitative determination of 15-20 elements in a matter of minutes. The technique, however, requires thin film samples and, therefore, subject to contamination from sample preparation procedures. To fully exploit the potential of this technique, we have set up (i) a clean room to prepare biological and environmental thin film samples with minimum contamination due to preparation and contact with other items and reagents, (ii) semi-automated sample preparation stations in the clean room so that samples doped with internal standards can be prepared as fast as they can be analyzed using a multi-sample analysis chamber (typically 6-12 samples/hour). The procedure employed in sample preparation involves making a homogeneous suspension or solution from the sample and spraying the doped preparation on a carbon or 1/7 mil mylar film using a very fine spray nebulizer. Past or current research projects in our trace element laboratory include the following

- a) Comparative studies of various trace element concentrations in normal and leukemic whole human blood. These studies showed severe deficiency of Fe, Cu and K and an enhancement of Zn in leukemic blood. These differences are qualitatively understood. Levels of chromium were also seen to be quite different in normal and diseased blood. The latter fact is not understood.
- b) Different cancerous lymph node specimens show very different trace element concentrations, not all of which are easily understood in terms of the physiologic differences in the different tumors.

c) Comparison of hair, finger nail and whole blood specimens from the same donor to see if these are equivalent indices of levels of various trace metals in the body. At least qualitatively, finger nails and hair show the same trace element composition as blood. The qualitative similarity between blood and hair is being exploited in examining the history of exposure of human subjects to toxic trace elements such as Pb, Hg, Sb, Cd, and As by scanning the full length of their hair for various trace elements as a function of distance from the root. It appears that even one time (short-term) exposure to rare heavy metals such as bismuth, are recorded in hair. Currently such analyses are being performed in our laboratory to study the history of exposure of 10-12 year old children in a high air pollution area.

d) Trace element analyses of recycled water samples are being performed to study the suitability of this water for general consumption at various times of the day and week.

Proton Ion Microprobe Applications to Biomedical and Environmental Sample Analysis

Z. H. Cho and J. Verba^{*} Laboratory of Nuclear Medicine and Radiation Biology, Electrical Sciences & Eng. Dept., Univ. of Calif., L.A.

With the increasing need for microscopic analysis of composition and structure of biological samples, have come developments of very high resolution electron microscopes and microprobes. Albert V. Crewe, *et al.*¹ has recently shown the feasibility of viewing single atoms with an electron microscope of resolution $\leq 3\text{\AA}$.

Development has begun on proton and other ion microprobes. The machines developed to date, are mainly low energy, $<25\text{ keV}$. They make possible the study of complete elemental composition at $2\text{--}3\text{ }\mu\text{m}$ resolution mass spectrometer analyzing atoms sputtered from the sample's surface. The range of data from such a machine far exceeds that from electron devices, which measure the number of transmitted or reflected electrons or x-ray fluorescence. Resolution, however, is more limited and also the analysis destroys the sample.

Higher energy ion microprobes would make possible the taking of new kinds of data on a microscopic scale. If x-ray fluorescence results are desired, 1 to 10 MeV ions have the advantages over electrons of having larger x-ray yield to damage ratio (heavy ions have been found to produce multiple vacancies in target atoms) and of producing much lower Bremsstrahlung background radiation. For thick samples, high energy ions have two advantages.

^{*}Now at Dept. of Radiology, Univ. of California, San Diego.

¹A. V. Crewe, M. Issacson, D. Johnson, *Nature* 231 (1971) 262.

They penetrate thicker samples with less change in path direction than electrons do. And from the well established dependence of stopping power on Z and density, information on internal composition can be obtained from energy loss data. A technique of reconstructing a 3-Dimensional image from energy loss measurements of beams transmitted through a sample in various places at various angles has been developed at U.C.L.A.²

High energy ion microprobes do not, as yet, have submicron resolution. Focusing the beam is a formidable task. Beam diameters of 10 to 15 μm have been obtained from U.C.L.A. using a 2 MeV Van deGraaff and quadrupole focusing,³ and 4 μm beams have been obtained at Harwell. Besides focusing, the beam spot size is dependent on the ion source size. Levi-setti,⁴ at Chicago, has carried out initial studies on a field ionization source for ions which has a size of under 10 $\text{\AA}$. He has obtained several tens of nanoamperes of beam current from the source using H_2 gas.

In conclusion, high resolution high energy ion microprobes would provide a valuable new tool for the elemental analysis of biomedical and environmental samples. Work is underway on the development of such microprobes, and progress is quite promising.

Air Pollution Research Objectives Using Trace Element Analyses

Richard C. Ragaini, Lawrence Livermore Lab., U. of Calif., Livermore

This workshop is concerned with the evaluation of research methods for environmental information. The focus is on present successes and limitations of nuclear methods in assessing energy related environmental problems. In this context, I will formulate future research objectives for trace element analyses as used in air pollution studies. Since aerosol sampling and analysis are intimately connected, this discussion will also include objectives in aerosol sampling techniques as well as the broader questions associated with trace-element aerosol chemistry. The accuracy and precision of the multi-element nuclear analytical techniques of neutron activation analysis, x-ray fluorescence analysis are acknowledged to be adequate for the proposed objectives and therefore no technique distinctions will be made.

² Z. H. Cho, General View on 3-D Image Reconstruction and Computerized Transverse Axial Tomography, in IEEE Trans. on Nuclear Science, NS-21, No. 3 (1974) 44.

³ Z. H. Cho, M. Singh, and A. Mohabattizadeh, in IEEE Trans. on Nuclear Science, NS-21, No. 1 (1974) 218.

⁴ R. Levi-setti, Enrico Fermi Institute, University of Chicago.

The measurement of trace metals in aerosols has received more attention in recent years because of an increasing concern over health effects from long-term exposure to toxic species and because of advances in elemental detection capabilities. Although the toxicity of materials depends on their physical and chemical states and their synergistic and antagonistic interactions, elemental analysis provides needed information on the total elemental concentrations in all their physical and chemical forms.

The most important needs with regard to trace elements in aerosols are: (1) accurate determinations of the impact of trace elements on man and the environment, (2) development of techniques utilizing trace elements as atmospheric emissions and dispersion markers for improvement of predictive capabilities for source emissions, (3) evaluation of emission control systems on stationary and mobile sources of toxic and noxious species. Because of their accuracy and sensitivity for many elements, the multielement nuclear techniques can be used to provide high quality information which can be used to characterize source emissions, to determine transport mechanisms, to investigate aerosol chemistry, and to determine the fate of trace species. Only after these data are understood can adequate biological impact assessments be made.

To accomplish these goals, aerosol measurements in pollution situations should follow a comprehensive design. Baseline or background aerosol measurements should be carried out in order to evaluate the natural background before the introduction of anthropogenic species. These baseline measurements serve as indicators of long-range aerosol transport mechanisms, of worldwide and regional aerosol levels outside of local pollution areas, and for evaluation of sites for location of potential stationary pollution sources. Complete chemical and physical characterization of source emissions should be carried out on a generic basis. A detailed knowledge of source emissions coupled with reliable plume dispersion codes will serve to aid air resource agencies in urban and/or industrial areas for pollution predictions and emission control strategies. Generic assessments of sources should be based on fuel composition, stack-emission controls, operational procedures (both routine and non-routine), meteorology and local topology. The intelligent use of generic source emission measurements in this way could be reinforced by selective field sampling stations. This approach would obviate the need for expensive, and possibly unnecessary ground-level air sampling networks.

Of course ambient air sampling should be utilized in all areas of interest. Precise measurements of aerosols should be correlated with all the relevant meteorological, operational and environmental parameters (including gaseous emissions) necessary for complete source characterization. These measurements are needed to evaluate the amount, rate, chemistry, and the impact of secondary aerosol production. Compared to source emission

characterization, the field of secondary aerosols by its nature is more complicated and requires much effort to reach a level of understanding necessary for emission regulations. These data are quite relevant to the whole question of ambient air standards versus source emission standards for public health. Particle-size measurements should of course be carried out downwind of sources at varying distances to evaluate elemental depositions, transport mechanisms, and secondary aerosol physics and chemistry. Ground-level sampling using stationary and/or mobile samplers and airborne sampling should be incorporated into any complete air sampling experiment. Diurnal and seasonal measurements should be performed to determine the importance of local meteorology relative to the importance of operational procedures.

One of the most important research objectives for determination of biological impact is the chemical characterization of trace elements in aerosols. Multielement nuclear analytical techniques can be used in this regard only when preceded by appropriate chemical separations based on different oxidation states and chemical forms of the elements of interest. Other related instrumental techniques such as x-ray photoelectron spectroscopy, and electron microprobe techniques should be developed to provide additional elemental and chemical information.

Thus, nuclear analytical techniques can play a significant role in the evaluation of total dose to man of trace elements in aerosols. By the documentation of elemental concentrations in ambient air according to particle size and chemical state, determinations of the inhalation doses can be carried out. The use of these techniques to measure the elemental abundances in the foodstuffs in man's diet and in the drinking water lead to the determination of the ingestion doses. Finally the techniques of neutron activation analysis and x-ray fluorescence analysis to document element concentrations in human tissues help to delineate the body burden for these species and the correlation of their concentrations to diseases and other health effects. For these reasons I believe that nuclear trace elemental analysis will play a significant future role in the evaluation of the impact of aerosols on human health and the environment.

PART III. APPENDIX

A. Statements by Persons Unable
to Attend the Workshop



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL ENVIRONMENTAL RESEARCH CENTER

CINCINNATI, OHIO 45268

June 14, 1974

4676 Columbia Parkway
Cincinnati, Ohio 45268

Dr. J. William Nelson
Department of Physics
The Florida State University
Tallahassee, Florida 32306

Dear Dr. Nelson:

Thank you for your recent invitation to participate in the workshop, "Nuclear Techniques for Environmental Trace Element Information Relative to Energy Production and Consumption," to be held at the Florida State University on June 24-26, 1974. Unfortunately, my laboratory schedule and personal commitments will prevent my participation in the workshop.

Our staff is very interested in the applicability of nuclear techniques, particularly X-ray fluorescence, to the characterization of drinking water. At the present time we are conducting a 15-month survey of 100 drinking water supplies, located in 35 cities in the U.S. These supplies have been selected as representative of the various supplies in our nation.

We need to determine the occurrence of trace element contaminants in drinking water to develop criteria for standards and to guide other health effects research. Since X-ray fluorescence is a rapidly developing technology we would appreciate guidance from those scientists working in this field as to what can and cannot be accomplished effectively with this technique.

We have a definite need for determining the following elements in 5100 samples (each 500 ml in volume) with the sensitivity indicated: Cr, Co, Ni, Cd, Pb (50.1 ppb); Na, K, Ca, V, Mn, Fe, Cu, Zn, Mo, Ag, I (21 ppb). In addition, data for F, Mg, Si, As, and Se with ppb sensitivity and for Li with 0.1 ppb sensitivity would be helpful.

- 2 -

Dr. J. W. Nelson for the following elements in the 0.1 ppb range in 350 of the 5100 elements would also be helpful in establishing the drinking water standards: B, Be, Sc, Ga, Ge, Br, Nb, Sr, Y, In, Sn, Sb, Te, Ba, W, Hg, Tl, Ra, and U. One- to four-liter water samples would be available for this part of the survey.

If you or John Rhodes have an opportunity to communicate these needs to the participants at the workshop, we will be very grateful. Any information that the participants may provide us relative to the applicability and sensitivity of X-ray fluorescence technology to the determination of the specified elements in drinking water will be deeply appreciated.

Sincerely yours,

Nancy S. Ulmer

Nancy S. Ulmer
Research Chemist
Criteria Development Branch
Water Supply Research Laboratory

cc: J. R. Rhodes

ENVIRONMENTAL RESEARCH & TECHNOLOGY, INC.



ROBERT S. HARLAN, JR.
Western Region Manager
3855 Birch Street
Suite 201
Newport Beach, California 92660
(714) 840-2584

June 6, 1974

Professor J. William Nelson
Department of Physics
The Florida State University
Tallahassee, FL 32306

Dear Bill:

The invitation for me to participate with the National Science Foundation Workshop "Nuclear Techniques for Environmental Trace Element Information Relative to Energy Production Consumption" is very much appreciated.

This confirms my telephone conversation with your Mrs. Nancy Conley that I will regretfully not be able to attend. This year, I am already obligated to work with the National Academy of Sciences on the committee to review the air quality criteria for oxidants and ozone.

However, I do feel very strongly that your workshop on particulate matter is very important and I would like to nominate in my place a colleague from ERT, Dr. Fran Berlandi. He can manage the time to attend. Dr. Berlandi is heading up our laboratory in Lexington and is highly qualified to participate in the discussions on the topics listed in the preliminary program. The following are my comments on topics I recommend for inclusion in your report to NSF.

Despite the progress that has been made in trace element monitoring and modeling source contributions and atmospheric processes from the data, the means to obtain data in a timely fashion are still quite primitive. On-line monitoring of particulate matter composition is likely to be needed for managing emission control programs. Dr. Dzubay may be discussing the system made available to EPA through their sponsored development at one of the national AEC laboratories. Beyond that it would be important for the workshop to specify a broad set of criteria which remain to be satisfied and to encourage the commercial development of analogous systems.

Professor J. William Nelson
June 6, 1974
Page Two

The main limitation of the x-ray fluorescence is its capability for determining total element content only while the sources and their various impacts, especially on health, are related to the chemical combination of the elements. It will be quite important to devise monitoring systems which are capable of providing continual data on species such as sulfate, nitrate, ammonium, and characteristic functional groups associated with organic compounds such as carboxylic acid, carbonyl, hydroxyl, nitro, and amino.

Among the sulfates, especially, it would be important to distinguish further which are in the form of sulfuric acid, ammonium sulfate, and other sulfates including complexes such as zinc ammonium sulfate. It would be important to distinguish water soluble from insoluble sulfates. The solubles are likely to be mainly anthropogenic while the insolubles would be mainly from windblown dust and fly ash. To meet such objectives the workshop may want to consider the status of chemical processing techniques which lead to decomposition of sulfates followed by the detection of SO₂ by a flame photometric detector.

The applicability of various spectroscopic techniques such as infrared Fourier spectroscopy for the direct observation of particulate matter collections is also worthy of consideration. It is important to identify the major problems that need resolution before this technique could receive wider application and be built in to an on-line monitoring system.

The proper selection of collection media is basic to all sensing techniques. This problem is further confounded when seeking information about particle size dependent composition as a function of time. No single medium meets all desired criteria. Therefore, it seems necessary that there be initiated a substantial effort, by a group with both practical and theoretical know-how, to produce a handbook that would guide optimization. Your workshop might further wish to consider listing those specifications for collection media which still need to be developed.

Please send further communications concerning this conference directly to Dr. Fran Berlandi at our address in Lexington, Massachusetts. When available I would certainly be pleased to receive directly from you, a report of the workshop.

With best personal regards to you and your family.

Sincerely yours,

Peter K. Mueller, Ph.D.
Technical Manager
Western Region

cc: Dr. F. Berlandi



STATE OF FLORIDA
DEPARTMENT OF POLLUTION CONTROL
2562 EXECUTIVE CENTER CIRCLE, EAST
MONTGOMERY BUILDING, TALLAHASSEE, FLORIDA 32301

PETER P. BALJET
EXECUTIVE DIRECTOR

July 15, 1974

W. D. FREDERICK, JR.
CHAIRMAN

Dr. John W. Winchester
NSF Workshop
Department of Oceanography
Florida State University
Tallahassee, Florida 32306

Dear Dr. Winchester:

I wish to thank Florida State University for the invitation to the Department to send a representative to the NSF Workshop on nuclear techniques for environmental trace element analysis. Although the techniques covered are beyond the scope of activity for this State agency, the knowledge acquired of the available processes and that Florida State University is in the forefront of research of on nuclear techniques for trace element analysis is of significant value.

From the practical point of view, State activity in this area will have to await directions from the U.S. Environmental Protection Agency. Until such time and in other areas, a mutually beneficial line of communications between Florida State University and the Department of Pollution Control is needed. In these areas where resources permit, we look forward to working with you in an exchange of information.

In this regard, you referred during the workshop to a possible need for information in our data bank. Please feel free to contact Mr. Bates Fountain or myself at 488-1345 in the future for assistance in this area.

Sincerely Yours,

Raymond S. Gregory
Raymond S. Gregory

RSG/js

John R. Middlemas
BOARD MEMBER

Mark D. Hollis
BOARD MEMBER

Alice C. Weinwright
BOARD MEMBER

Y. E. Hall
BOARD MEMBER

Current Status and Priorities of Analytical
Technique Development*

Jerome J. Wesolowski** Air and Industrial Hygiene Laboratory,
Laboratory Services Program, State of Calif. Dept. of Health

This talk will delineate the current status and priorities of Analytical Technique Development for Urban Smog research. We will discuss what pollutants are normally measured in urban smog research programs, what specificities, sensitivities, accuracies, etc. are needed for these measurements in order to reach the specific objectives of the programs, what is the current status of the techniques needed for this research, and what are the priorities for future analytical technique development efforts.

During the presentation a number of recommendations will be made regarding the general area of analytical techniques development. Some of these are based on the data listed in Tables 1 and 2 which are attached.

The following recommendations are reproduced here in order that the participants may have an opportunity to read them before the meeting thus allowing for more active participation during the discussion periods. They are not necessarily listed in order of priority.

1) More effort should be placed on determining the equivalency and accuracy of methods, particularly with respect to the chemistry of the aerosol. Specifically the equivalency of the more common methods presently in use for the determination of sulfur compounds in ambient air aerosol should be determined. Table 3 categorizes some of these methods. "Direct" refers to methods which require little manipulation of the sample whereas "indirect" refers to wet chemical methods.

2) Improvements are needed in the methods for the measurement of gaseous NH_3 and specific hydrocarbons.

3) Methodology must be developed for sulfuric acid mist, Pt and Pd.

4) Improvements are needed in the methods for SO_4^{2-} , NO_3^- , NH_4^+ , specific particulate carbon compounds, and H_2O .

5) It would be useful to determine the degree of equivalence between the determination of total sulfur in ambient air aerosol as

* Submitted for presentation of "Chemical and Physical Interactions of SO_x , NO_x , and Photochemical Oxidant: Current Status and Priorities in Research, Berkeley UC-ARB Conf., March 18-19, 1974.

**Although Dr. Wesolowski was not able to attend the Workshop he submitted these remarks for inclusion in the Report.

measured by a simple rapid method such as x-ray fluorescence analysis and water soluble sulfate as obtained by the more time consuming wet chemistry.

6) More effort should be placed on determining the quantitative and qualitative usefulness of ESCA for aerosol characterization.

7) High priority should be given to the development of a method which semi-continuously determines the sulfur content of aerosol at nanogram levels. One such system that shows promise is the thermal-flame photometric detector system.

8) There should be further work to determine the usefulness of the thermal-flame ionization detector combination which obtains the concentration of carbon species in aerosol as a function of their volatility.

9) There is a need to develop a reference multi-stage aerosol impactor, that is, one which has negligible bounce off and wall loss and for which the effective cut-off diameters are well known.

10) In many cases the largest error in the determination of the chemistry of the aerosol is the sampling error, not the analytical error. Therefore, for those agencies responsible for funding research on improvements in methodology more emphasis should be placed on improvements in aerosol sampling.

11) More emphasis should be placed on research to develop substrates for collecting aerosol that minimize both the analytical and the sampling errors.

12) High priority should be given to develop a size segregating sampler for aerosols of diameters below 0.5 microns which provides sufficient sample for chemical analysis.

13) Development of "in situ" methods for chemical analysis of aerosols should be emphasized since errors associated with the collection of the aerosol play such a dominant role.

14) To better understand aerosol formation mechanisms it is important to determine the spatial distribution of chemical species in individual particles. Therefore, development of such physical methods as the ion microprobe should be conducted.

15) The quantitative value of elastic scattering of ions (e.g. alpha particles) for determining light elements such as carbon, oxygen, and nitrogen in aerosol should be studied.

16) The quality rather than the quantity of the data should be stressed. Thus it is recommended that atmospheric research proposals not be considered for funding unless they contain a quality assurance section which clearly delineates what tests and procedures will be undertaken to assure the funding agency of the quality of the data obtained. Approximately one out of every five dollars spent on atmospheric research will have to be used to carry out the necessary quality assurance effort. It is simply not true that bad data is better than no data at all.

Gas	Detection Limit Required (ppm)	Present Capability		Technique* Development Priority
		Technique	Detection Limit (ppm)	
SO ₂	0.005	FPD	0.005	low
O ₃	0.005	Chemiluminescence	0.005	low
NO	0.005	Chemiluminescence	0.001	low
NO ₂	0.005	Chemiluminescence	0.001	low
CO	0.1	Catalytic Reduction/FID	0.1	low
H ₂	0.001	Chemiluminescence	0.001	high
		Microwave Resonance	0.001 (?)	
		H ₂ SO ₄ bubbler	0.005	
Specific HC	0.001	GC/FID	0.01	high

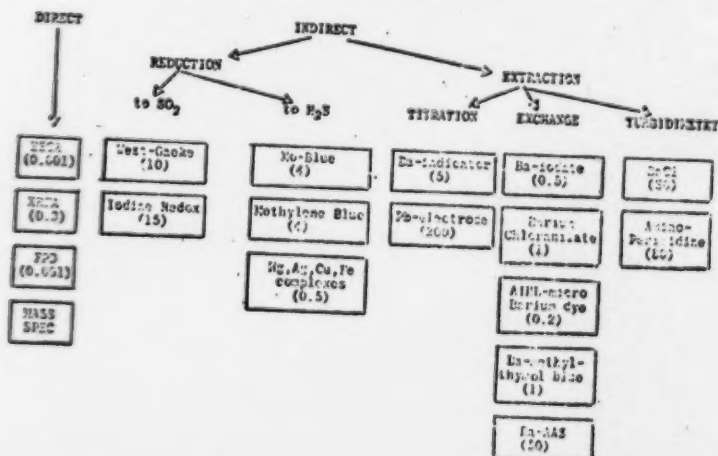
*This estimated priority is based on the sensitivity, accuracy, and specificity required.

TABLE II
BASIC AEROSOL MEASUREMENTS
SEMICONTINUOUS AS A FUNCTION OF PARTICLE SIZE
FOR URBAN AIR QUALITY RESEARCH

Aerosol	Detection Limit Required (µg)	Present Capability		Technique* Development Priority
		Technique	Detection Limit (µg)	
H ₂ SO ₄	0.01	Humidified nephelometer Microdiffusion (Coulman)	-- 10	high
SO ₄ ²⁻	0.01	ESCA AHL Micro-technique	0.005 0.1	high
NO ₃ ⁻	1	Micro-xyleneol	1	moderate
NO ₃ ⁺	1	Indophenol-blue	10	high
Total Sulfur	0.01	FPD, XRF	0.01, 0.3	high
Carbonaceous material	0.001-1	ESCA Thermal-FID Mass Spec	0.005 1 0.001	high
Pb, Br	1	XRF	0.005	low
Ka, Cl, Al	1	NAA	0.001	low
V	0.01	XRF, NAA	0.03, 0.001	moderate
Pt, Pd	0.01	AAS	20, 3	high
H ₂ O	5	Microwave waterometer	5	high
Mass	100	B-gauge Gravimetric	10 25	moderate

*The estimated priority is based on the sensitivity, accuracy, and specificity required.

TABLE III
CLASSIFICATION OF METHODS
FOR INORGANIC SULFUR COMPOUNDS IN AEROSOLS



Notes: Numbers in parentheses are the lower limit of detection in µg.

B. Outline of the Workshop

- 0900 Opening remarks: J. W. Nelson
- 0915 Welcome: Robert A. Spivey, Provost, College of Arts & Sciences, FSU
Steve Edwards, Chairman, Department of Physics, FSU
- 0930 Monday morning, Session A--Chairman: R. Akselsson
Rapporteur: V. P. Guinn
- 0930 A1. Air pollution research objectives using neutron activation analysis: Vincent P. Guinn
- 1000 A2. Trace element importance in Environmental Protection Agency program goals: William E. Wilson
- 1030 COFFEE
- 1050 A3. Trace element importance in Atomic Energy Commission program goals: Hodge R. Wasson
- 1120 A4. Air pollution research at Tennessee Valley Authority: C. Huang
- 1330 Monday afternoon, Session B--Chairman: W. H. Christie
Rapporteur: H. van Rinsvelt
- 1330 B1. Keynote address--Analytical chemical needs in air pollution research: A. P. Altshuller
- 1410 B2. Analytical methods for baseline measurements: John A. Cooper
- 1440 TEA
- 1500 B3. Design of a program for interlaboratory comparison of analytical results: David C. Camp
- 1530 B4. Design of specialized air sampling equipment for trace element studies using nuclear techniques: J. William Nelson
- 1600 TOUR OF THE FSU ACCELERATOR LABORATORY--Kenneth R. Chapman
- 1730-1930 COCKTAILS at home of J. W. Nelson, 2306 Domingo Dr. (576-2521)

0900 Tuesday morning, Session C--Chairman: C. Orsini
Rapporteur: L. Newman

0900 C1. Environmental information from intensive air particulate size fraction trace element studies: John W. Winchester

0930 C2. Concepts for a large scale aerosol collection and analysis system: Joseph M. Jaklevic

1000 C3. Air pollution research planning for energy systems in the Northeast: Bernard Manowitz

1030 COFFEE

1050 C4. Significance of remote marine aerosol studies in energy impact assessment: Dennis L. Meinert

1120 C5. Environmental sampling in remote continental aerosol studies: Nolan Mangelson

1330 Tuesday afternoon, Session D--Chairman: David Johnson
Rapporteur: K. Hardy

1330 D1. Power plant impacts on the urban aerosol: Ernest S. Gladney

1400 D2. Trace element studies of fossil fuels: Robert Ristinen

1430 TEA

1450 D3. Trace element distributions in aerosols near highways: Thomas A. Cahill

1520 D4. PIXE applications to automotive and industrial aerosol health effects: Roland Akselsson

1600 D5. Accelerator methods in rain water and filter brushing measurements: Bernard Cohen

1900 DUTCH TREAT DINNER at Joe's Steak House and Lounge, 1713 Mahan Dr.

0900 Wednesday morning, Session E--Chairman: R. Walter
Rapporteur: T. Cahill

0900 E1. Water pollution research objectives using x-ray methods
of trace element analysis: John Rhodes

0930 E2. Biomedical trace element research: P. Ong

1000 E3. Environmental factors in trace metals in human health
problems: R. K. Jolly

1030 COFFEE

1050 E4. Proton ion microprobe applications to biomedicine:
Z. H. Cho and J. Verba

1120 E5. Standardized computer interfacing for nuclear information
using CAMAC: R. A. LaSalle

1330 Wednesday afternoon--Drafting of workshop report of steering
committee with conference rapporteurs

Steering Committee: J. W. Nelson (workshop chairman)
J. W. Winchester
R. Akselsson

Rapporteurs: V. P. Guinn
H. van Rinsvelt
L. Newman
K. Hardy
T. Cahill

C. List of Persons Attending the Workshop

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Richard Weickowicz
Bureau of Planning
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